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CONTENT OF HEAVY METALS IN THE SOIL OF AGRICULTURAL AREAS: CASE STUDY AT BACHOK, KELANTAN, MALAYSIA

by

NUR SHUHADA YUSAIMEE

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School of Health Sciences

Universiti Sains Malaysia

Health Campus

16150, Kubang Kerian, Kelantan

Malaysia

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectrometry
Al	Aluminium
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
Cd	Cadmium
cm	Centimetre
Cr	Chromium
Cu	Copper
DOE	Department of Environmental
EPA	Environmental Protection Agency
Fe	Ferum
$FeCr_2O_4$	Chromite
GPS	Global Positioning System
HCl	Hydrochloric Acid
Hg	Mercury
HNO_3	Nitric Acid
L	Litre
mg	Milligram
Mn	Manganese
Ni	Nickel
Pb	Lead
SPSS	Statistical Package for the Social Science
um	Micrometre
WHO	World Health Organization
Zn	Zinc

ABSTRAK

Pengawalan jumlah kepekatan logam dalam tanah adalah sangat penting dengan mengambil kira faktor toksikologi manusia dan produktiviti pertanian. Objektif kajian ini adalah untuk menentukan kandungan logam berat Kuprum (Cu), Kromium (Cr), Kadmium (Cd), Plumbum (Pb) dan Mangan (Mn) dalam tanah kawasan pertanian di Bachok, Kelantan. Sebanyak 30 sampel tanah telah dikumpulkan pada kedalaman 0-20 cm menggunakan sampler tanah. Semua sampel telah dikeringkan dan menjalani proses penghadaman asid sebelum dianalisa menggunakan Spektrometri Penyerapan Atom (AAS). Dapatan kajian menunjukkan bahawa kepekatan logam berat dalam tanah kawasan padi berada pada turutan Pb>Cr>Cu>Cd>Mn dengan purata kepekatan masing-masing 0.319, 0.065, 0.037, 0.013 dan 0.009 mg/L. Manakala, kepekatan logam berat dalam tanah kawasan sayuran pula berada pada turutan Mn>Pb>Cr>Cd>Cu dengan purata kepekatan masing-masing 0.226, 0.153, 0.107, 0.006 mg/L dan tiada pengesanan kepekatan logam Cu. Walaubagaimanapun, kepekatan logam berat di kawasan kajian masih berada di bawah had piawai Jabatan Alam Sekitar (JAS), Malaysia. Walaupun kandungan kepekatan logam berat dalam tanah kawasan pertanian adalah dalam had selamat, kajian lanjut boleh dijalankan untuk mengenal pasti punca permasalahan logam berat di dalam tanah kawasan pertanian. Oleh itu, rawatan yang sewajarnya boleh diambil untuk mengurangkan pencemaran tanah dan sekaligus dapat menjaga kelestarian pembangunan pertanian.

ABSTRACT

It is important to realise that the soil is both a source of metals and also a sink for contaminants. The factors controlling the total and bioavailable concentrations of metals in soils are of great importance with regard to both human toxicology and agricultural productivity. The objective of this study was to determine the content of heavy metal Copper (Cu), Chromium (Cr), Cadmium (Cd), Lead (Pb) and Manganese (Mn) in the soil of agricultural areas at Bachok, Kelantan. A total of 30 samples were collected at a depth of 0-20 cm using a soil sampler. All samples were dried and undergo acid digestion prior to analysis using Atomic Absorption Spectrometry (AAS). The finding shows that the heavy metals concentration in soil of paddy area is in order of Pb>Cr>Cu>Cd>Mn with average concentration of 0.319, 0.065, 0.037, 0.013 and 0.009 mg/L and the heavy metals concentration in soil of vegetable area is in order of Mn>Pb>Cr>Cd>Cu with average concentration of 0.226, 0.153, 0.107, 0.006 mg/L and no detection of concentration of Cu. However, the heavy metal concentration is still below the standard limit of Department of Environmental (DOE), Malaysia. Although the results of heavy metals concentration in soil of agricultural areas are within the safe limits, further research can be carried out to identify the source of heavy metals in soil of agricultural areas. Thus, proper treatments can be taken to reduce soil contamination and to keep sustainable agricultural development.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Heavy metal contamination in the agricultural soils is of great concern because of possible influence on the productivity of these soils. Heavy metal pollution in soil is a component of environmental pollutant closely related to human activities. According to Wei and Yang (2010), the sources of the metals in agricultural soils may be derived from mining, sewage sludge, pesticides and fertilizers. About 90% of the pesticides are used on cotton, rice, oilseeds and horticultural crops (Li *et al.*, 1997). Some fertilizers and pesticides are known to contain various levels of heavy metals, including Cd and Cu (Kabata-Pendias & Pendias, 1992).

Excessive accumulation of heavy metals in agricultural soils may not only result in environmental contamination, but elevated heavy metal uptake by crops may also affect food quality and safety. Younas *et al.* (1998) stated that the contamination of fields by metallic elements and their aerial deposition is likely to result in a corresponding contamination of harvested crops and the impact on food consumers. The concern over soil contamination stems primarily from health risks, from direct contact with the contaminated soil, vapours from the contaminants, and from secondary contamination of water supplies within and underlying the soil. The contamination of agricultural soils can pose long term environmental and health implications (McLaughlin *et al.*, 1999; Mueller, 1994; Needleman, 1980). Hence, there is an increasing need to study heavy metal distribution and accumulation in agricultural soils (Li *et al.*, 1997).

The soil is a long-term sink for the group of potentially toxic elements known as heavy metals, including copper (Cu), chromium (Cr), cadmium (Cd) and lead (Pb). Whilst these elements display a range of properties in soils including difference in mobility and bioavailability, leaching losses and plant uptake are usually relatively small compared to the total quantities entering the soil from different diffuse and agricultural sources. As a result, these heavy metals slowly accumulate in the soil profile over long run. This could have long-term implications for the quality of agricultural soils, including the maintenance of soil microbial processes, phytotoxicity at high concentrations and the transfer of zoo toxic elements to the human diet from increased crop uptake or soil ingestion by grazing livestock (Nicholson *et al.*, 2003).

Intake of heavy metals via the soil-crop system has been considered as the predominant pathway of human exposure to environmental heavy metals in agricultural area (Liu *et al.*, 2007). According to numerous studies, the pollution sources of heavy metals in environment are mainly derived from anthropogenic sources. The anthropogenic sources of heavy metals in agricultural soils include mining, smelting, waste disposal, urban effluent, vehicle exhausts, sewage sludge, pesticides, fertilizers application and so on (Li *et al*, 2008).

1.2 Problem Statements

In many countries, soil contamination has become a serious problem with rapid development in industrialization. Among the most significant soil contaminants resulting from both natural and manmade sources, heavy metals are of prime importance due to their long-term toxicity effect. Metal content in soils is the combination of metals arising from human activities and natural processes. According to Pacyna (1986), addition of anthropogenic metals to the soil is much greater than contribution of metals from natural sources.

However, there are no studies about the soil pollution of heavy metal in Bachok, so far. This could have long-term implications for the biological, chemical and physical properties of agricultural and forest soil and its fertility as well as productivity (Nicholson *et al.*, 2003). Adomaitis *et al.* (2003) stated that the heavy metals Cr, Cd, Pb, Ni, Cu, Zn take part in the biological turnover and their excess or lack of disturbance of the metabolism and inhibited vegetation. Metals may bioaccumulate in living organisms and be transferred into the food chain (Bogaert *et al.*, 2000). Willaert *et al.* (1985) in his studies has confirmed that the major parts (75-80%) of heavy metals get into human organisms with vegetable diet when plants take it from the soil.

Therefore, this study was conducted to determine the content of heavy metals in agricultural soil in Bachok. In order to achieve that, the concentration of heavy metals in paddy and vegetable soil were assessed. Then, the results of the concentration of heavy metal in sampling point were compared with the standard limit of DOE.

1.3 Research Objectives

1.3.1 General Objective

To determine the concentration of heavy metals in the soil of agricultural areas

1.3.2 Specific Objectives

I. To determine the concentration of Cd, Cu, Cr, Mn and Pb in the soil of agricultural areas.

II. To compare the concentration of heavy metals in the soil of paddy and vegetable area.

III. To compare the concentration of heavy metals with the standard limit of DOE.

1.4 Hypothesis

Null Hypothesis:

There is no significant different of each Cd, Cu, Cr, Pb and Mn in soil at sampling point.

Alternate Hypothesis:

There is significant different of each Cd, Cu, Cr, Pb and Mn in soil at sampling point.

1.5 Significance of Study

Heavy metal pollution is much more common than most people realize. According to Zaini *et al.* (2013), there is still a dearth of studies on heavy metal pollution in Malaysia, particularly those related to soil pollution and its management. Determination of heavy metal is very important for monitoring environmental pollution. The presence of heavy metals in the environment that exceed permissible limit can cause adverse effects on human, animals and plants (Adedosu, 2013).

Determining the concentration of heavy metals in soil of agricultural area is important due to its potential harmful effects to human health and environment. Agriculture soil serves as a vital function in food production. Majority of the population in the case study area grow paddy and vegetables as a source of income and food sources in their daily life. Therefore, the presence of heavy metals in agriculture soil may become threat to the population through food consumption. Study shows that, consuming or exposed to heavy metal can cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system and acute or chronic damage to the nervous system (Njar *et al.*, 2012).

This study will also serve as a future reference for researchers on the subject of heavy metals contamination in agricultural soil. And importantly, this study will provide the information of standard limit of heavy metal in agricultural soil by DOE and hopefully it can helps local authority in their responsibility to take care of the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal

Heavy metals are natural components of the earth's crust. Heavy metal which also known as toxic metal are refers to any metallic element that has a relatively high density, high atomic number and atomic weight, and is toxic or poisonous event at low concentration. Lead (Pb), mercury (Hg), and cadmium (Cd) are some examples of heavy metals element. Heavy metals cannot be degraded or destroyed. They generally exhibit good electrical and thermal conductivity when in their pure form.

Heavy metals permeate into our bodies through the air, food and drinking water. As trace element to maintain the metabolism of the human body, some heavy metals are important. However, any excess of these metals can lead to poisoning. Long-term exposure to heavy metals can cause chronic disease and death to human.

2.1.1 Copper (Cu)

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper. For instance it is applied in the industries and in agriculture. According to Lenntech (2015), copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production.

When copper ends up in soil it strongly attaches to organic matter and minerals. Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. That is why on copper-rich soils only a limited number of plants have a chance of survival.

2.1.2 Cadmium (Cd)

Cadmium is found naturally in the environment. It is released into the environment through mining and smelting, its use in various industrial processes, and enters the food chain from uptake by plants from contaminated soil or water. Cadmium has been widely dispersed into the environment through the air by its mining and smelting as well as by other man-made routes, which are usage of phosphate fertilizers, presence in sewage sludge, and various industrial uses such as NiCd batteries, plating, pigments and plastics (ATSDR, 2008). Cadmium is also present in cigarette smoke, and smoking doubles the average daily intake.

Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the human as cadmium can accumulate in our bodies, especially when we eat multiple plants.

2.1.3 Chromium (Cr)

Chromium is not found as a free element in nature but is found in the form of ores. The main ore of chromium is chromite ($FeCr_2O_4$). Chromium is an essential trace element, but hexavalent chromium (Cr (VI)) is very toxic and carcinogenic. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry.

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur.

2.1.4 Lead (Pb)

Lead is a naturally occurring element found in small amounts in the earth's crust. It can be found in all parts of our environment such as the soil, the water, and the air. There are many ways that humans can be exposed to lead. Among the major sources are lead-based paint, leaded gasoline, lead-contaminated water, manufacturing of lead batteries, rubber products, glass and other lead-containing products, and lead oxide fumes that result when demolishing industrial buildings (USEPA, 2015).

Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, and also in entire food chains. These will experience health effects from lead poisoning. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present.

2.1.5 Manganese (Mn)

Manganese compounds exist naturally in the environment as solids in the soils. Through the application of manganese pesticides, manganese will enter soils. In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms. For instance disturbance of the division of water to hydrogen and oxygen, in which manganese plays an important part. Manganese can cause both toxicity and deficiency symptoms in plants. When the pH of the soil is low manganese deficiencies are more common. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leafs and brown spots on leaves. Deficiencies can also cause these effects. Between toxic concentrations and concentrations that cause deficiencies a small area of concentrations for optimal plant growth can be detected.

2.2 Soil

Soil is an important constituent of human biosphere. According to Yaylali-Abanuz (2011), the soil is not only a geochemical reservoir for the contaminants, but also a natural buffer for the transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass. Similarly, agriculture soil serves as vital functions in our life, especially for food production. It is essential to protect this source and ensure its sustainability.

Soil pollution is the presence of toxic chemicals (pollutants or contaminants) in soil in high enough concentrations to be of risk to human health and/or ecosystem. Additionally, even when the levels of contaminants in soil are not of risk, soil pollution may occur simply due to the fact that the levels of the contaminants in soil exceed the levels that are naturally present in soil (in the case of contaminants which occur naturally in soil).

Soil pollution often caused by accidental releases of chemicals or the improper disposal of hazardous wastes. Increased inputs of metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in the developing country has lead to large-scale pollution of the environment. These chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters, and human health (Yaylali-Abanuz, 2011).

The initial sources of heavy metals in agricultural soils are the parent materials from which the soils were derived, but the influence of parent materials on the total concentrations and forms of metals in soils is modified to varying degrees by pedogenetic processes (Herawati *et al.*, 2000). In areas affected lightly by human activities, heavy metals in the soils derived mainly from pedogenetic parent materials, and metals accumulation status was affected by several factors such as soil moisture and management patterns. A research conducted in Gansu province, China, by Li *et al.* (2008) concluded that the main factor for heavy metals accumulation was lithological factor in three arid agricultural areas. It is reported that soil aqua regia soluble fraction of Co, Ni, Pb, and Zn were highly correlated with soil Al and Fe. These elements were associated with indigenous clay minerals in the soil high in Al and Fe.

Furthermore, the main reason why the soil becomes contaminated is due to the presence of man-made waste. Wei and Yang (2010) stated that heavy metals pollution in soil may be due to traffic emission, industrial emission, mining, sewage sludge, pesticides and fertilizers.

Industrial activity has been the biggest contributor to the problem in the last century, especially since the amount of mining and manufacturing has increased. Most industries are dependent on extracting minerals from the earth. Whether it is iron ore or coal, the by products are contaminated and they are not disposed off in a manner that can be considered safe. As a result, the industrial waste lingers in the soil surface for a long time and makes it unsuitable for use.

There are different sources of metal contamination in mining areas, including grinding, concentrating ores and tailings disposal (Adriano, 1986; Wang *et al.*, 2004). Inappropriate treatment of these tailings and acid mine drainage could pollute the agricultural fields surrounding the mining areas (Williams & Lei, 2009). Take Tongling copper mine in Anhui province in China as an example, metal mining had been an important economic base in this area from ancient time. The major mining areas have been concentrated in a narrow star-shaped basin called Fenghuang Mountain. Long-term mining activities in this area had caused widespread metal pollution. The soil concentration of average total Cu was 618 mg kg-1, with a wide range of 78-2830 mg kg-1. Lead concentration in soil also showed a large variability with a mean of 161 mg kg-1. The total Zn concentration varied from 78 to 1280 mg kg-1, with an average of 354 mg kg-1 (Wang *et al.*, 2004). It was reported that the majority of the agricultural soils were contaminated with As. High As concentration in these soils may be attributed to arsenopyrite which is known to occur in many areas of Southeast Asia, especially in tin mining regions (Patel *et al.*, 2005).

Chemical utilization has gone up tremendously since technology had provided the modern pesticides and fertilizers. They are full of chemicals that are not produced in nature and cannot be broken down by it. As a result, they seep into the ground after they are mixed with water and slowly reduce the fertility of the soil. Other chemicals damage the composition of the soil and make it easier to erode by water and air. Plants absorb many of these pesticides and when they decompose, they cause soil pollution since they become a part of the land.

Heavy metals input to arable soils through fertilizers courses increasing concern for their potential risk to environmental health. Lu *et al.* (1992) reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers, and much attention had also been paid to the concentration of Cd in phosphate fertilizers. However the concentration of Cd in both phosphate rocks and phosphate fertilizers from China was in general much lower than those from the USA and European countries. It should be concerned that although the contents of toxic metals in most of the fertilisers in China were lower than the maximum limits, the trace elements input to agricultural land were still worth concern, since the annual consumption of fertilizers accounted to 22.2, 7.4 and 4.7 × 106 tons for N, P and K fertilizers (in pure nutrient), respectively (Luo *et al.*, 2009).

Traditionally, agriculture has been the main base of the economies in this region. In some of the countries mentioned above, phosphatic fertilisers have been used for long periods. For instance, the great majority of agricultural soils in Malaysia are heavily fertilized by this kind of fertilizers, which was reported by Zarcinas *et al.* (2004). Regression analysis resulted in that log aqua regia soluble As, Cu, Cd, and Zn in soil are significantly correlated with log aqua regia soluble P. Soils in these southern Asian countries have P requirements, so that histories of P fertilizers addition, with associated with impurities (Cd, Cu, As, and Zn), seem to be greater on these countries (Zarcinas *et al.*, 2004).

Agricultural use of pesticides was another source of heavy metals in arable soils from non-point source contamination. Although pesticides containing Cd, Hg and Pb had been prohibited in 2002, there were still other trace elements containing pesticides in existence, especially copper and zinc. It was estimated that a total input of 5000 tons of Cu and 1200 tons of Zn were applied as agrochemical products to agricultural land in China annually (Luo *et al.*, 2009).

According to Alloway (1990), rapid development of industry and increasing release of agrochemicals into the environment has lead to growing public concern over the potential accumulation of heavy metals within agricultural soil. This has been supported by Tahmineh *et al.* (2013) which stated that heavy metal contamination in soil is a major concern due to its toxicity and threat to human life and the environment. Vegetables take up heavy metals by absorbing them from contaminated soils or from atmospheric deposition from polluted air. Chronic low-level intake of heavy metals has a negative effect on the health of humans and other animals, and no known medical treatment is able to reverse these health effects (Huang *et al.*, 2007).

2.3 Previous Study

2.3.1 International Studies

Wei and Yang (2010) found that the agricultural soils in China are significantly contaminated by Cd and Hg, which derived from anthropogenic activities. The sources of Cd and Hg in China agricultural soils may be mainly originated from pesticides and fertilizers. However, the agricultural soil in China is lowly contaminated by the other metals.

The study done by Shan *et al.* (2013) indicated that most of the studied metals (Fe, Mn, Cu, Ni, Pb, Zn, Cd, Cr and Co) in arable soils of the study area were shown to have low concentrations, except for Cd (0.241 mg kg−1). According to the results of the PCA analysis, Fe, Mn, Pb, Zn, Cd, and Co formed the first component (PC1) explaining 40.1 % of the total variance. The source of these metals was attributed to farming practices ("anthropogenic" factor). Cu, Ni, and Cr fell into the second component (PC2), heavy metals that derived from parent rock materials ("lithogetic" factor). This component describes 24.6 % of the total variance. Compared to paddy lands, soils in drylands had greater accumulations of all the metals in PC1, which can be explained by a higher rate of phosphorus fertilizer application and a longer farming history.

Nicholson *et al.* (2003) has conducted a study of an inventory of heavy metal inputs (Zn, Cu, Ni, Pb, Cd, Cr, As and Hg) to agricultural soils in England and Wales in 2000, which accounting for major sources including atmospheric deposition, sewage sludge, livestock manures, inorganic fertilisers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts. Across the whole agricultural land area, atmospheric deposition was the main source of most metals, ranging from 25 to 85% of total inputs. Livestock manures and sewage sludge were also important sources, responsible for an estimated 37–40 and 8–17% of total Zn and Cu inputs, respectively. However, at the individual field scale sewage sludge, livestock manures and industrial wastes could be the major source of many metals where these materials are applied.

Previous studies reported by Khumoetsile *et al.* (2012) showed that Zn, Cu, Pb, Co, and Ni are present in the soil as a result of human activities, whereas Fe, Al and Mn are due to natural processes. Besides, this preliminary study had provided a scientific basis for studies on contamination and control and further monitoring of the heavy metal accumulation in the soils of Botswana. If heavy metals contamination in soils is properly monitored, remediation measures can be put in place to avoid detrimental effects on soil productivity.

2.3.2 Local Studies

A study done by Nurainisyamimi *et al.* (2013) in determining of heavy metal Fe, Mn, Cr and Ni in paddy soil showed that the amount of heavy metals in the soil is high and exceed the permissible limit. Fe recorded the highest average concentration (61528.71 ± 44577.70) mg/kg followed by Cr (970.69 ± 1368.40), Mn (917.51 ± 1032.00) and Ni (686.92 ± 970.54) mg/kg respectively. Heavy metal concentration of Ni and Cr exceed the critical limit as stated by Kabata-Pendias (2011).

The study done by Khairiah *et al.* (2012) in determining the heavy metal, Pb, Cd, Cu, Zn, Fe, Mn and Cr content in paddy soils at KETARA, Besut, Terengganu, Malaysia were extracted using the sequential extraction method, which consists of four fractions namely the easily leachable and ion exchange (EFLE), acid reducible (AR), oxidizable organic (OO) and resistant (RR). Heavy metals were detected using an inductively coupled plasma mass spectrometer (ICP-MS). The study showed that Fe was the most dominant metal whereas Cd had the lowest concentration for all studied soil types. With the exception of Fe and Mn, the soils were naturally low in the respective heavy metals (Zn, Cu, Cr, Pb, and Cd). The high amount of soil Fe and Mn in the studied soils could be attributed to the occurrence of Fe-Mn hydrous-oxide mottles. Meanwhile, the higher levels of Mn in the ELFE and AR fractions suggest that the continuous usage of agrochemical materials for paddy cultivation activities, rendered high bioavailable Mn in the soils. The elevated levels of Pb and Cd in the soils could possibly be attributed to anthropogenic sources.

The study conducted by Yap *et al.* (2009) in several rice fields near Marudu, Sabah, Malaysia indicate that the highest mean percentage recorded for the soils of Kota Marudu were as follows: organic carbon (8.02%), grain size (85.92%) and soil pH (5.91). Mn occurred in the highest concentration in the non-litogenic fraction of the soil in all the areas studied.

Ripin *et al.* (2014) has conducted a study regarding on the concentration of 5 heavy metals (Cu, Cr, Ni, Cd, Pb) in the soils around Perlis, to assess heavy metals contamination distribution due to industrialization, urbanization and agricultural activities. Finding shows that overall concentrations of Cu, Cr, Ni, Cd and Pb in the soil samples ranged from 0.38-240.59, 0.642-3.921, 0.689-2.398, 0-0.63 and 0.39-27.47 mg/kg respectively. The concentration of heavy metals in the soil display the following decreasing trend: Cu>Pb>Cr>Ni>Cd. From this result, found that level of heavy metal in soil near centralized Chuping industrial areas give maximum value compared with other location in Perlis. The Pollution index revealed that only 11% of Cu and 6% of Cd were classes as heavily contaminated. Meanwhile, Cu and Pb showed 6% from all samples result a moderately contaminated and the others element give low contamination. Results of combined heavy metal concentration and heavy metal assessment indicate that industrial activities and traffic emission represent most important sources for Cu, Cd and Pb whereas Cr, Ni mainly from natural sources. Increasing anthropogenic influences on the environment, especially pollution loadings, have caused negative changes in natural ecosystems and decreased biodiversity.

CHAPTER 3

METHODOLOGY

3.1 Background of Study Location

This study was conducted at agricultural areas of vegetable and paddy, which are located at Bachok. Bachok is situated in Kelantan, Malaysia, and its geographical coordinates are North 6° 4' 0", East 102° 24' 0". Traditionally, agriculture has been the main base of the economies apart from fishing and business in this study area. 10 random sampling points were pointed out to collect the soil samples, which is 5 soil samples were collected from crop soil and the other 5 sample were collected from paddy soil. The latitude and longitude of the point were determined using Global Positioning System, GPS (Table 3.1).

Table 3.1: Position of sampling point at study location

Sampling point	Paddy soil	Vegetable soil
A	6°00'45.5"N, 102°22'54.2"E	6°03'30.4"N, 102°23'25.0"E
B	6°00'45.5"N, 102°22'54.7"E	6°03'30.2"N, 102°23'24.7"E
C	6°00'46.0"N, 102°22'54.2"E	6°03'30.6"N, 102°23'25.0"E
D	6°00'46.0"N, 102°22'54.6"E	6°03'30.5"N, 102°23'24.7"E
E	6°00'45.8"N, 102°22'54.4"E	6°03'30.5"N, 102°23'24.9"E

3.2 Study Design

Quantitative method was used throughout the study. The concentration of Cd, Pb, Cr, Cu and Mn were measured for each soil sample taken. Samples were taken at Bachok which is at the agricultural area of paddy and vegetable.

3.3 Sampling Method

The soil samples were taken randomly at two sampling points. Each soil sample were taken at the depth between 0-20 cm from the top using a soil sampler and kept in plastic bag. The samples were then brought to the laboratory for further analysis, includes sample drying, sample digestion and heavy metal extraction. This experiment used acid digestion method, which is 0.25 g of dry soil sample was digested with HCl and HNO_3. The samples were analysed in the Forensic Science Laboratory, Universiti Sains Malaysia, Kampus Kesihatan, Kubang Kerian.

3.4 Study Instruments

All instruments and apparatus used in this study were summerized in Table 3.2

Table 3.2: List of instruments and apparatus used in the study

Instruments and Apparatus	Brand
Beakers 250 mL, volumetric flask 50 mL	SCHOTT DURAN
Whatmann filter paper (diameter, 110 mm)	Whatman
Hot plate	ERLA
Pipette 5 uL	Gilson, France
Digital electronic balances	Shimadzu ATX224
Soil sampler	Ward'S
Hot oven sterilizer	Memmert
Atomic Absorption Spectrometer	PerkinElmer

3.5 Data Collection

3.5.1 Primary Sources

The samples were taken at paddy and vegetable area in Bachok (Table 3.1). The sampling session was done within three weeks, from April 2015 until May 2015 on the dry season. First sampling session is on 19th April 2015, second sampling session is on 26th April 2015 and the last sampling session is done on 3rd May 2015.

3.5.2 Lab Preparation

Prior when to the sampling area, the tools such as soil sampler was ensure to be clean from any dirt. To make sure that the soil sample taken would have less contamination with other materials. During laboratory work, all apparatus used also were cleaned first as it might affect the heavy metal concentration in the sample.

3.5.3 Sample Preparation

30 soil samples were collected in a range of 0-20 cm depth using the soil sampler. The position of the sampling points was noted by using GPS. The soil samples were air dried in the oven at 105°C for 24 hours and crushed using pestle and mortar. Any gravel, stones and plants fragments were removed to obtain a homogenous sample. The stones and plant fragments were removed by passing the sample through a 5 um sieve. The powdered samples were stored in plastic bottles. Samples preparation and digestion was referred to Khumoetsile, Alfred and Gilbert, (2012).

3.5.4 Sample Digestion

0.25 g of sample was weighed into 250 mL beaker and digestion was carried out on a hot plate in a fume chamber avoiding splattering all through. 50 mL deionized water, 0.5 mL concentrated HNO_3 and 5.0 mL concentrated HCl were added to each samples. Digestion was continued until the entire volume was reduced to about 15 mL. The beakers were allowed to cool to room temperature. The digests were then filtered into 50 mL volumetric flask and made up to 50 mL volume with deionized water. After that, the digest was filtered to remove silica content, through an ashless 110 mm diameter Whatmann type 41 filter paper, England, and transferred to universal bottle.

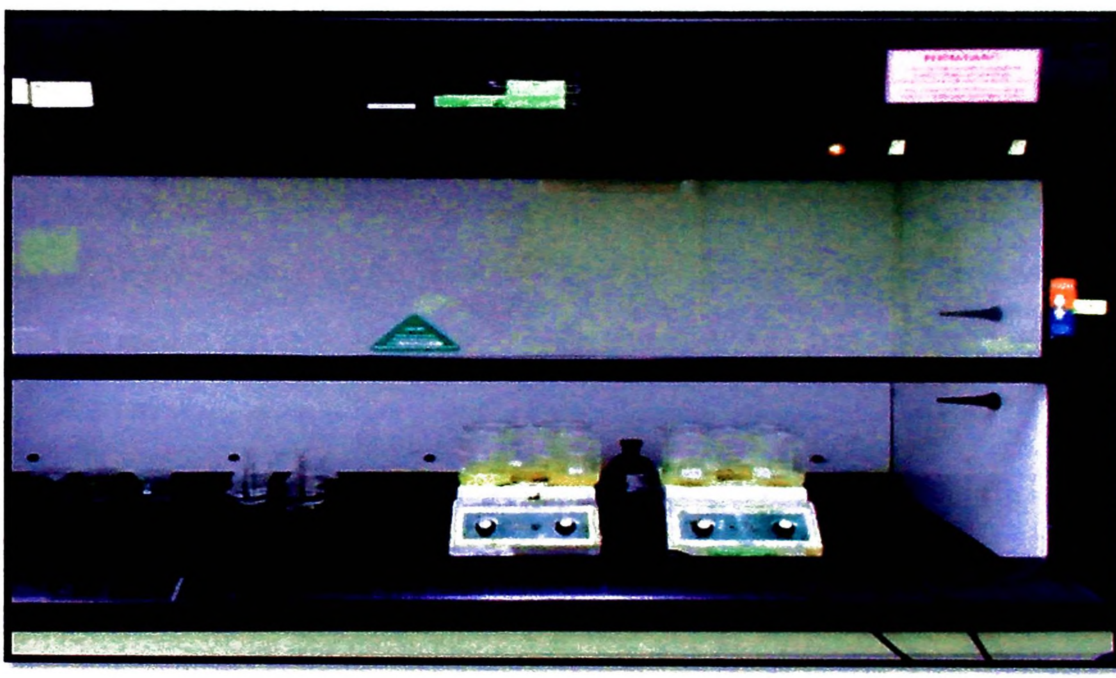

Figure 3.1: Digestion was carried out in fume chamber

Figure 3.2: Samples are filtered using Whatmann filter paper

3.6 Quality Control (QC) Sample

Quality control samples are required for any sampling and analysis program. Without quality control information, the quality of the environmental data collected can be neither evaluated nor qualified. In order to assure that a test run is valid and the results are reliable, quality control samples were used in the performance of the analysis.

As in this study, Instrument blank is used as QC samples. A blank is deionized water which is treated as a sample. It is used to minimise the effect of carry-over from the previous sample during the analysis. Before analysing the sample, blank was run first and then followed by the samples. Sample analysis was started with the low concentration to the high concentration of the sample. This is to ensure that the element come from the sample itself and not the carry-over from the previous sample.